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The First Fullerene−Metal Sandwich Complex: An Unusually Strong Electronic Communication between Two C_{60} Cages

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Bisfullerene compounds have received considerable attention due to their potential for future optical and electronic applications.[1] In particular they provoke an interesting topic concerning possible electronic communication between the two C_{60} units through the spacer. Insertion of conjugated[2] or electroactive[3] organic spacers transforms the hybridization of C_{60} carbon atoms involved in the spacer binding from sp^2 to sp^3, and thus the conjugation is not retained between the C_{60} and spacer moieties. A weak, through-space electronic communication has been observed only in the cases of $C_{120}O$,[4] $C_{120}(CH_2)_2$,[5] and $C_{120}C$,[6] where the fullerenes are directly bonded to each other or are separated by a single carbon spacer. This through-space electronic communication via overlapped π-orbitals from separate cages vanishes when even a two-carbon spacer such as $-C{\equiv}C-$ is inserted between the two C_{60} centers.[7] On the other hand, the study on the electronic communication between the C_{60} molecules through the metal spacer has been thus far precluded by lack of a fullerene metal sandwich complex. The coordination of two, electron-withdrawing fullerenes on a single metal center seems to be energetically unfavorable. Multiple fullerene coordination may be realized with a metal cluster when it has enough electron-donating ligands to compensate for the electron-withdrawing effect of the C_{60} units. Furthermore, metal cluster−C_{60} complexes with a face-capping cyclohexatriene-like μ_3-η^2,η^2,η^2-C_{60} have demonstrated an unusual thermal and electrochemical stability as well as strong electronic communications between the metal cluster and C_{60} centers.[8] These considerations prompted us to investigate the interaction between the electron-rich $Rh_6(CO)_{12}(dppm)_2$ cluster compound and C_{60}. Herein we report the synthesis and structural characterization of the first C_{60}−metal sandwich complex, which exhibits a strong electrochemical interaction between the two C_{60} centers through a metal cluster spacer.

Reaction of $Rh_6(CO)_9(dppm)_2(\mu_3$-η^2,η^2,η^2-$C_{60})$ (**1**)[9] with excess C_{60} in refluxing chlorobenzene for 3 h formed a new green compound identified by analytical TLC (silica gel), which could not be further characterized because of its marginal solubility after solvent removal. The reaction mixture was in situ treated with 1 equiv of CNR ($R = CH_2C_6H_5$) at room temperature for 90 min. Removal of the solvent and purification by preparative TLC (silica gel, $CS_2/CH_2Cl_2 = 7/1$, $R_f = 0.3$) provided green solid **2** as the major product (30%). Compound **2** showed increased solubility and was formulated as $Rh_6(CO)_5(dppm)_2(CNR)(C_{60})_2$ on the basis of microanalytical and NMR spectroscopic data.[10]

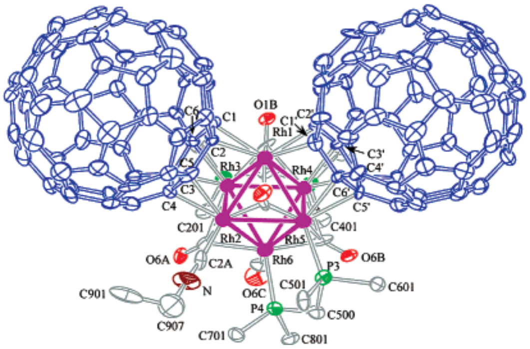

Figure 1. Molecular geometry and atomic-labeling scheme for **2**. Phenyl groups except ipso carbons on dppm and RNC ligands are omitted for clarity.

The molecular structure of **2** is shown in Figure 1.[11] The octahedral metal framework Rh_6 is retained, and the two μ_3-η^2,η^2,η^2-C_{60} ligands are face-capping Rh(1, 2, 3) and Rh(1, 4, 5) triangles, respectively. The coordination environments of the two C_{60} ligands are different from each other; the Rh(1, 2, 3) triangle is coordinated by an isocyanide ligand and a phosphorus atom of a dppm ligand, while the Rh(1, 4, 5) triangle is coordinated by two phosphorus atoms, each from the two dppm ligands. Interestingly, the Rh1 atom is bonded to both of the face-capping C_{60} ligands in an η^2-mode, which is the first example of a metal atom connecting two C_{60} cages. Although the Rh1 atom is coordinated by two electron-withdrawing C_{60} ligands, the Rh1−C (C_{60}) bond distances (Rh1−C1 = 2.19(2) Å; Rh1−C2 = 2.20(1) Å; Rh1−C1′ = 2.14(2) Å; Rh1−C2′ = 2.15(2) Å) are comparable to the other Rh−C (C_{60}) distances (average 2.19 Å) in **2**. The ligated C_6 ring of the C_{60} ligand on the Rh(1, 2, 3) triangle exhibits alternation in C−C bond distances (average 1.40 and 1.49 Å, respectively), but no systematic bond alternation is observed either in the C_6 ring of the other C_{60} ligand or in the Rh−C (C_{60}) distances. Overall, the bonding parameters for the μ_3-η^2,η^2,η^2-C_{60} ligands are similar to those in other related cluster systems.[8,12] An electron-donating terminal CNR ligand is observed on the Rh2 atom that is coordinated to the electronegative fullerene. One dppm ligand bridges the Rh3−Rh4 edge and the other dppm ligand the Rh5−Rh6 edge. Compound **2** has a terminal carbonyl ligand on the Rh6 atom and four face-capping μ_3-CO ligands. One μ_3-CO ligand is capping the Rh(4, 5, 6) triangle which is trans to the C_{60} coordinated Rh(1, 2, 3) triangle. The three remaining μ_3-CO ligands are disposed in a fashion to form a tetrahedron composed of four μ_3-CO ligands as observed in $Rh_6(CO)_{12}$-$(dppm)_2$.[13]

Electrochemical properties of **2** have been examined by cyclic voltammetry, and cyclic voltammogram (CV) of **2** is shown in Figure 2. The CV of **2** exhibits six well-separated reversible, one-electron redox waves localized at C_{60} cages, and half-wave

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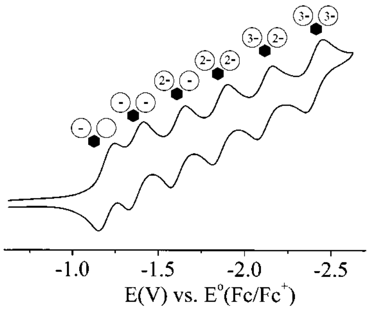

Figure 2. Cyclic voltammogram of **2** (scan rate = 10 mV/s).

Table 1. Comparison of the Half-Wave Potentials (V vs Fc/Fc$^+$) of C_{60} and **2** in Chlorobenzene with Tetrabutylammonium Perchlorate as the Supporting Electrolyte

C_{60}		2	
$E_{1/2}^1$	−1.06	$E_{1/2}^1$	−1.19
		$E_{1/2}^2$	−1.38
$E_{1/2}^2$	−1.43	$E_{1/2}^3$	−1.62
		$E_{1/2}^4$	−1.86
$E_{1/2}^3$	−1.91	$E_{1/2}^5$	−2.12
		$E_{1/2}^6$	−2.41

potentials ($E_{1/2}$) for free C_{60} and **2** are summarized in Table 1. Each redox wave of **2** corresponds to sequential, pairwise addition of six electrons into the two C_{60} centers to form $C_{60}^{-}-Rh_6-C_{60}$, $C_{60}^{-}-Rh_6-C_{60}^{-}$, $C_{60}^{2-}-Rh_6-C_{60}^{-}$, ..., and ultimately $C_{60}^{3-}-Rh_6-C_{60}^{3-}$. Three redox waves ($E_{1/2}^1$, $E_{1/2}^3$, and $E_{1/2}^5$) are shifted to more negative potentials relative to free C_{60} because of Rh_6 to C_{60} back-bonding. The parent molecule $Rh_6(CO)_{12}(dppm)_2$ exhibits an irreversible, one-step two-electron reduction of the Rh_6 cluster center at −1.96 V and two consecutive oxidation steps (−1.42 and −1.29V) for the dianionic species.[9] The absence of the Rh_6 cluster reduction wave for **2** in the solvent window could be explained by significant decrease in electron affinity of the cluster framework due to coordination of two, electron-rich polyanionic C_{60} ligands, which are generated during electrochemical studies. This observation suggests an electronic communication between the cluster and C_{60} centers. There is little difference between donor effects of a phosphine ligand and a benzyl isocyanide ligand in C_{60}−metal cluster complexes, which lead to the negative shifts (0.08−0.09 V) of C_{60} reduction potentials compared to the parent carbonyl complex; $Os_3(CO)_9(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[8a] $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[8a] $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$,[9] and $Os_3(CO)_8(C_6H_5CH_2NC)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$[9] exhibit a C_{60}-localized first redox wave ($E_{1/2}^{0/-1}$) at −0.98, −1.06, −1.07, and −1.06 V, respectively. These data indicate that the donor effect of a phosphorus end of a dppm ligand is comparable to that of a benzyl isocyanide ligand. Therefore, the electronic environment for the two C_{60} centers is very similar despite the difference in coordination spheres around the two C_{60} centers. In this context, the large peak separations ($\Delta(E_{1/2}^1, E_{1/2}^2) = 0.19$ V, $\Delta(E_{1/2}^3, E_{1/2}^4) = 0.24$ V, $\Delta(E_{1/2}^5, E_{1/2}^6) = 0.29$ V) in the three redox pairs of the two C_{60} ligands reflect an unusually strong electronic communication between the two C_{60} centers via the Rh_6 spacer. Our results contrast sharply with very small peak separations ($\Delta(E_{1/2}^1, E_{1/2}^2) = 0.04$ V, $\Delta(E_{1/2}^3, E_{1/2}^4) = 0.06$ V, $\Delta(E_{1/2}^5, E_{1/2}^6) = 0.14$ V) observed for $C_{120}O$,[4] which exhibits the strongest through-space interactions reported thus far in bisfullerene compounds. In compound **2**, the long distance (d(C1−C2′) = 3.60 Å; d(C2−C1′) = 3.51 Å) between the two C_{60} centers limits π-orbital overlap of separate C_{60} cages, and thus the contribution of the through-space electronic communication is expected to be negligible. The second redox wave in each pair in the CV's of **2** and $C_{120}O$ becomes increasingly separated from the first wave as the reduction proceeds, presumably due to the effects of increasing Coulombic repulsion between the two C_{60} moieties.[4]

The first C_{60}−metal cluster sandwich compound described here should serve as a model compound for two carbon nanotubes connected by a heterogeneous inorganic junction, which might find useful applications in future electronic materials. Efforts are currently underway to understand the exact nature of bonding between the metal spacer and C_{60} cages that has led to a strong electronic communication between the two C_{60} centers.

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Supporting Information Available: Synthesis of **1**, CV's of $Os_3(CO)_8(RNC)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$, $Os_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2,\eta^2,\eta^2\text{-}C_{60})$, and $Rh_6(CO)_{12}(dppm)_2$, UV−vis spectra of C_{60}, $Rh_6(CO)_{12}(dppm)_2$, **1**, and **2**, and details of the crystallographic studies of **1** and **2** (PDF) as well as an X-ray crystallographic file for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) See Supporting Information.

(10) IR (CS_2) ν_{CO} 1987 (s, br) cm^{-1}; ^{1}H NMR (1,2-$C_6D_4Cl_2$, 298K) δ 8.4−6.9 (m, 45H), 5.33 (m, 1H), 5.06 (AB pattern, 2H, J = 16.7 Hz, $CNCH_2C_6H_5$), 4.90 (m, 1H), 4.57 (m, 1H), 3.96 (m, 1H); ^{31}P{^{1}H} NMR (1,2-$C_6D_4Cl_2$, 298 K) δ 18.3−12.9 (m, 3P), 5.96 (m, 1P). Anal. Calcd for $C_{183}H_{51}O_5NP_4Rh_6$: C, 71.25; H, 1.67; N, 0.45. Found: C, 71.08; H, 2.01; N, 0.46. Attempts to obtain mass spectroscopic data (FAB$^+$, FAB$^-$, and MALDI TOF) have not been successful.

(11) Crystallographic data for $\mathbf{2}\cdot 2.75CS_2\cdot 1.5C_6H_4Cl_2$: monoclinic, space group $P2_1/n$, a = 17.59(3) Å, b = 23.98(5) Å, c = 31.90(6) Å, β = 96.75(4)°, V = 13360(45) Å^3, Z = 4; crystal size 0.78 × 0.40 × 0.04 mm^3. Diffraction data were collected at 293 K on a Bruker SMART diffractometer/CCD area detector. The structure was solved by direct methods and refined by full-matrix least-squares analysis to give R = 0.0848 and R_w = 0.2290 (based on F^2) for 1766 variables and 18 592 observed reflections with $I > 2\sigma(I)$ and $1.29 < \theta < 23.00$.

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